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A Liquid Nitrogen Immersion Cryostat for Optical Measurements

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*But apart from the increasing cold, the weather remained
remarkably stable and free from gales.*

— Alfred Lansing

Endurance. Shackleton's Incredible Voyage

Abstract

A liquid nitrogen immersion cryostat has been developed for optical measurements. Liquid nitrogen in the sample chamber is kept free of bubbles and schlieren by the use of a cooling jacket of sacrificial liquid nitrogen, which is kept at a lower pressure than the sample chamber. This design has proven especially useful for volatile liquid samples, where direct electrical connections, rapid sample freezing, and efficient heat dissipation are required, but it can also accommodate a wide variety of other samples. The cryostat is compact, easy to use, and relatively inexpensive.

Introduction

It is often useful to conduct optical spectroscopic experiments at cryogenic temperatures, as absorption features are usually narrower and more sharply resolved at low temperatures, sample degradation is slowed, and it is often possible to trap unstable intermediates. Optical experiments are often performed at liquid helium temperatures, but liquid helium experiments are complex and expensive, and liquid nitrogen temperature (around 77K) suffices for many applications. Optical cryostats are commercially available, for example from Janis¹, Oxford², and MMR Technologies³, and these either use a cold-finger or a gas heat exchange design. For a cold-finger system, the sample holder is cooled through its mechanical attachment to a cooling element, which is cooled by a variety of means including boiling liquid nitrogen, boiling liquid helium, or Joule-Thompson cooling. The sample holder and cooling element need to be surrounded by a guard vacuum of less than 5 mTorr to minimize heat transfer through the surrounding air. In the gas heat exchange design, the sample is surrounded by cooled vapor, which is either a static exchange gas independent of the cryogen or is vapor from the cryogen.

Several aspects of the cold-finger design present problems for many experiments: *i*) liquid samples need to be in a well sealed sample holder to prevent evaporation and/or bubbling prior to freezing and upon application of the guard vacuum; *ii*) samples are

cooled relatively slowly, often causing glass-forming solvents to crystallize or solutions to precipitate; *iii*) it is difficult to precisely control the sample temperature, especially in the presence of sample heating by absorption of light or electrical impedance; *iv*) electrical connections to liquid or frozen samples are difficult due to the fact that the holder needs to be sealed; and *v*) exchanging samples requires a half-hour or longer since the vacuum needs to be released, and often the entire cryostat needs to be warmed. Gas heat exchange cryostats solve many of these problems since the sample space is at atmospheric pressure and the sample is surrounded by cold vapor. However, the cooling rate is often too slow, and the evaporation rate too high for certain samples. For example, we were unable to perform vibrational Stark effect measurements effectively^{4,5} until the development of the cryostat design described below.

Confronted with these difficulties, we have developed a liquid nitrogen immersion cryostat for optical measurements which has most of the same advantages as the gas heat exchange design, but also allows for very rapid sample cooling. The principle difficulty with liquid immersion cryostats is distortion and scattering of light by cryogen bubbles and schlieren⁶. This was solved by surrounding the sample chamber by a jacket of sacrificial liquid nitrogen which is at lower pressure than the nitrogen in the sample chamber⁷. The sacrificial nitrogen in the jacket boils continuously, but is not a problem since it is out of the optical path. A cryostat which is functionally similar but structurally quite different was designed by Lõhmus and coworkers for high pressure optical measurements⁸.

Description of the cryostat

A schematic view of the immersion cryostat is shown in Figure 1⁹. The vacuum shroud and instrument skirt were purchased from Janis Technologies (SuperTran model) and used without modification. As these parts are not cooled, rubber O-rings are used to seal the windows and the different sections of the external assembly; calcium fluoride, potassium bromide, and other delicate window materials all work well. Inside the vacuum chamber are three concentric tubes: a thin wall, polished aluminum tube which serves as a radiation shield and does not hold a pressure difference; a stainless steel tube which creates the outside of the liquid nitrogen cooling jacket; and a stainless steel tube

which forms both the inside of the nitrogen jacket and the outside of the sample chamber. The inner tube has a 3.8 cm diameter, which sets the maximum size of a sample. The stainless steel tubes connect at the bottom in a window assembly, which was machined from a single piece of stainless steel, and which holds two 25 mm diameter optical

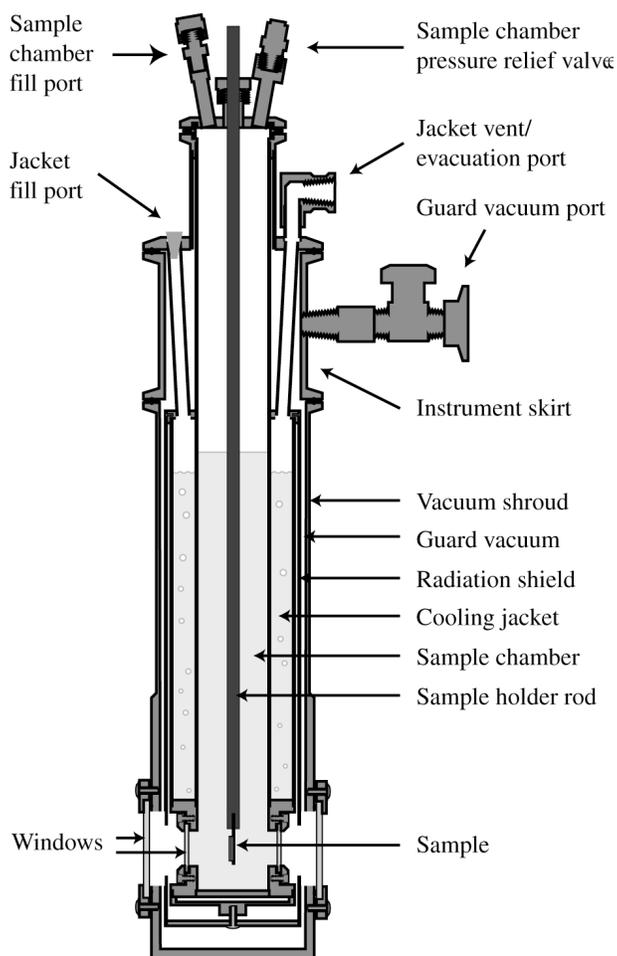


Figure 1. Schematic diagram of the optical immersion cryostat, shown in 1/4 scale.

windows in place in the front and back, sealed with indium wire. The cooling jacket extends down the sides of the window assembly and below the window assembly for maximal cooling and to speed the initial cool-down. The bottom of the window assembly has caps for both the sample and the jacket regions. With the exception of the radiation

shield, which is held in place by bolts, all metal to metal connections were made by either welding or brazing.

For the internal windows, which separate the sample chamber from the guard vacuum, Cleartran¹⁰ (Janos Technology), broad-band anti-reflection coated Cleartran (Spectral Systems), and fused silica windows (CVI Laser Company) have all been used successfully, whereas calcium fluoride windows (Janos) tended to crack upon repeated cooling. The windows were installed in a uniform manner, by tightening screws gradually and in an alternating pattern, to avoid optical depolarization due to strained crystals. Depolarization with the fused silica windows at 800 nm is below 1%¹¹. The clear aperture diameter is 19 mm, leading to an optical access of f/1.3. The sample is suspended from a hollow 0.64 cm diameter fiberglass rod which is partially filled with epoxy glue, and which also serves as a conduit for electrical connections. Samples can be immersed quickly for rapid freezing and can be exchanged in only a few minutes, or much faster if a second sample holder rod is used.

The cryostat has been used in two different modes, both of which eliminate bubbles in the sample chamber and optical path: *i*) with the sample chamber at atmospheric pressure and the jacket at reduced pressure, and *ii*) with the jacket at atmospheric pressure and the sample chamber at elevated pressure. For the former situation, the cooling jacket is continuously pumped with a diaphragm pump¹², thereby lowering the boiling point in the jacket and lowering the temperature of both regions. In this manner, the sample temperature is typically around 74K, but can be lowered to 64K with sufficient pumping. Bubbles are prevented because the liquid nitrogen in the sample chamber is at atmospheric pressure and is cooled to several degrees below its boiling point (77 K at 1 atm.). In the second mode, the nitrogen jacket is left open to the atmosphere, which simplifies refilling and removes the need for a diaphragm pump. When a sample is immersed and the sample chamber is sealed, the sample chamber pressure naturally builds, which rapidly stops all bubbling. Initial excess pressure is relieved with a 10 psi pressure relief valve, but there is no loss of nitrogen in the sample chamber during stable operation. In either configuration, about 10 minutes are required

for initial cool-down and optical measurements can be made within a minute of sample immersion.

The nitrogen hold time is approximately 6 hours before refilling is required, and the nitrogen regions can be refilled as often as desired. This is particularly important for applications where long-term signal averaging under constant conditions is required. When the sample region is filled, the liquid nitrogen is filtered through a paper filter to remove any suspended snow due to condensed water.

Infrared transmission of the cooled cryostat, using anti-reflection coated Cleartran windows, is about 80% over most of the mid-infrared region, with the rest of the light being lost due to reflection losses from the windows. Also, liquid nitrogen has a weak absorption band at 2345 cm^{-1} ¹³, but the 4.3 cm pathlength in the sample chamber results in absorption of over 90% of the light between 2310 and 2385 cm^{-1} . For situations where this particular frequency is of interest, liquid oxygen has been used successfully as a cryogen, accomplished by condensing oxygen into the cryostat from a gas cylinder. Both the nitrogen and oxygen used had sufficient water either dissolved or suspended in the cryogens to be apparent in the infrared spectra, but this was not sufficient to cause significant problems in those regions of the spectrum or to lead to any observable scattering at other frequencies.

Acknowledgements

The immersion cryostats were machined by the Stanford University Department of Physics machine shop and welded and brazed by Manuel Gutierrez at the Hansen Experimental Physics Laboratory tube shop. Thomas Treynor and Eun Sun Park assisted in the testing of the cryostats. This work was supported by grants from the NSF Chemistry and Biophysics Divisions.

Afterward

While this chapter was in publication, we officially disclosed the design to the Stanford Office of Technology Licensing, who determined that it was not financially

sensible to patent it. As a result, the plans were given to Janis Research Company without charge, so the invention could be optimized by professionals and would be easily available to other researchers. Janis is currently in process of improving the design.

During the last year of cryostat use, a problem that has appeared is that users tend to over-tighten the bolts that hold the inner windows in place. These are size 2-56 bolts, which are not able to withstand high torques, resulting in broken bolts and expensive repairs to the cryostat. Even after repair, the tapped holes are inferior to other holes, leading to difficulty in getting good seals and avoiding optical depolarization. It is strongly suggested that the bolts are tightened only enough to cause a good seal, at which point there is moderate resistance to further tightening. If the user has never broken a bolt before, it would be a good idea to break one in a piece of scrap metal first.

References

- (1) Janis Research Company, 2 Jewel Drive, P.O. Box 696, Wilmington, MA 01887.
- (2) Oxford Instruments, Old Station Way, Eynsham, Witney, Oxon, OX8 1TL, U.K.
- (3) MMR Technologies Inc., 1400 North Shoreline Blvd. #A5, Mountain View, CA 94043.
- (4) E. S. Park, S. S. Andrews, R. B. Hu, and S. G. Boxer, *J. Phys. Chem. B* **103**, 9813 (1999).
- (5) S. S. Andrews and S. G. Boxer, *J. Phys. Chem. A* **104**, 11853 (2000).
- (6) When liquid He is pumped below its lambda point, it exhibits many desirable properties for optical measurements and such cryostats are widely used. Unfortunately these experiments are complex, costly and time-consuming. The present cryostat design offers many of the advantages of pumped He systems, though, of course, not the very low temperature.
- (7) Another technique for suppressing bubbles in liquid nitrogen is to gently flow helium vapor over the surface of the liquid. This simple but poorly known method is not as effective as the nitrogen jacket.
- (8) A. Lõhmus, A. Laisaar, A. Freiberg, A. Ellervee, V. Korrovits, R. Lõhmus, and M. Tars, *Czech. J. Phys., Suppl. S5* **46**, 2775 (1996).
- (9) Detailed schematics can be provided upon request.
- (10) Cleartran is water-free zinc sulfide, and is a trademark of CVD Inc.
- (11) On initial cooling, depolarization is minimized when the cryostat is filled slowly, which allows a gradual and uniform cooling of the windows.
- (12) Gast Manufacturing Inc., P.O. Box 97, Benton Harbor, MI 49023.
- (13) A. L. Smith, W. E. Keller, and H. L. Johnston, *Phys. Rev.* **79**, 728 (1950).